

Chapter 11: The Thermodynamic Definition of Entropy

Can all of the energy in the universe be converted into useful work?

11.1 Thermal Cycles Never Produce Work at 100% Efficiency

The efficient production and consumption of energy is central to the health of any society. Our society operates in a complex network of interrelationships that extend around the globe. Global energy use patterns have an impact on the quality of the environment, biological diversity, and the quality of life. Dysfunctional energy supply and consumption networks lead to global instability. The unequal distribution of energy resources produces disparity in wealth between the richest and poorest nations and the richest and poorest individuals within nations. This disparity gives rise to political unrest and instability. Dependence on imported fossil fuels increases our susceptibility to supply disruptions and price fluctuations caused by turmoil in developing regions. Economic disparity also contributes to environmental degradation.

Much deforestation can be traced to energy supply limitations. Historically, deforestation in places as diverse as the British Isles and the Near East was driven by the necessities of cooking fuel, shelter, and warmth. Currently, the search for alternative fuels, such as sugar cane, palm oil, and coconut oil is contributing to deforestation and soil depletion. Our current dependence on fossil fuels has resulted in the increase of greenhouse gases. The sustainable use of alternative fuels will decrease greenhouse gas emissions. Photosynthesis, especially in forests and oceans is the primary sink for CO_2 . Biofuels plantations are, however, often not managed in a sustainable manner, leading to infertile soils. Deforestation and the resulting growth of desert areas have a negative impact on the ability of the biosphere to absorb CO_2 . Biofuels production, deforestation, global climate change, and agricultural land degradation may interact to accelerate global warming. Competition for fertile soils and clean water also has a negative impact on food production.

We often focus on the use of energy for transportation, electricity, and industry. Energy in the form of food is even more important and basic. Throughout the globe, food is often in short supply. Water is a critical input for agriculture. Desertification and competition with energy crops decreases the supply of water and soil resources for food production. The lack of water for agriculture will further increase the disparities between the richest and poorest among us.

The careful analysis of energy efficiency is critical for the management of our economy. Historically, the first attempts to analyze energy efficiency came at the beginning of the era of steam power. Steam powered the industrial revolution. Steam engines are examples of processes that operate as thermal cycles, which convert heat transfers into useful work. The concept of entropy was introduced to understand the conversion of heat into work by steam engines. However, at no time in human history has the understanding of energy flow in our society been more important. The lessons from the 1850's are just as salient today as they were at the beginnings of the industrial revolution. For one reason, steam turbines are the primary method for the production of electricity. Steam turbines are engines that convert energy from burning coal, oil, wood, biomass, solar thermal energy, or nuclear energy into mechanical work. The work from thermal cycles can also be in the form of chemical work. Processes for solar thermal energy conversion of water into hydrogen are important examples. Steam engines, steam

turbines, internal combustion engines, and many other processes operating in closed thermal cycles share common limitations.

The successful understanding of thermal cycles was made possible by the development of a simple model of a steam engine, by Nicolas Léonard Sadi Carnot in 1824. The key to this model is to retain all the important aspects of an engine without unnecessary complications. Consider an engine, that operating in a cycle, converts heat energy into work. Can all of the energy that is supplied from a fuel to power the engine be converted into work?

Efficiency of Cyclic Processes - Carnot Cycles: An engine is any process that converts thermal energy into work. The working substance in an engine undergoes expansions and contractions that are used through mechanical linkages to do useful things. Steam is an important working substance. Internal combustion engines use air and the combustion products from burning fuels as the working substance. Refrigerators and heat pumps use Freons, ammonia, or small hydrocarbons, such as butane, as the working substance. Although we normally think of gases as the working substance, liquids and solids can also be used as a working substance. What do all engines, regardless of the working substance have in common? All engines extract energy by heat transfer from a high temperature reservoir, do work, and deposit waste energy by heat transfer into a low temperature reservoir, Figure 11.1.1a.

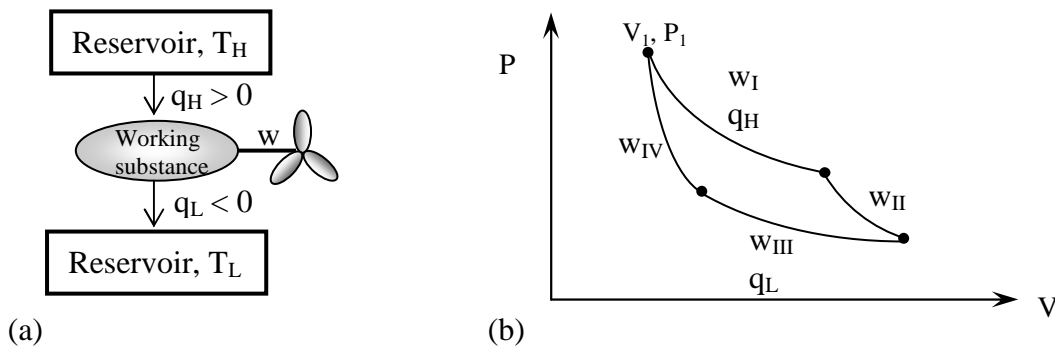


Figure 11.1.1: (a) A general process operates between a high temperature reservoir at T_H and a low temperature reservoir at T_L and performs work w . (b) A Carnot cycle extracts energy q_H from the high temperature reservoir, delivers waste heat q_L to the low temperature reservoir, and performs work, $w = w_I + w_{II} + w_{III} + w_{IV}$.

The temperature of the high temperature reservoir is T_H and the temperature of the low temperature reservoir is T_L . The high temperature reservoir is kept at constant temperature T_H by burning a fuel, be it coal, gasoline, or nuclear fuel. The nuclear fuel may be consumed in a fission reactor or in fusion processes in the sun. The low temperature reservoir is often the surroundings, so T_L is often near 298 K. Engines operate in a closed cycle. For example, refrigerators and heat pumps recycle their Freon instead of venting this working substance to the atmosphere. Because the working substance is recycled, the overall process must also work in a cycle. If the system starts at V_1 and P_1 , one complete cycle returns the system back to the initial state at V_1 and P_1 . The First Law applies to any process, so the total heat transfer and the total work done must be given by:

$$\Delta U = q + w$$

11.1.1

However, internal energy is a state function. The change in internal energy for each cycle must be zero, $\Delta U = 0$. A Carnot cycle is an idealized cycle that is chosen to produce maximal work when extracting energy q_H from the high temperature reservoir, Figure 11.1.1b. A Carnot cycle consists, starting at V_1 and P_1 , of an:

- I. isothermal expansion at T_H , extracting energy q_H from the high temperature reservoir,
- II. adiabatic expansion that cools the system from T_H to T_L ,
- III. isothermal contraction at T_L , depositing energy q_L into the low temperature reservoir,
- IV. and an adiabatic contraction that heats the system back to the starting temperature.

The total heat transferred and work done around the cycle sum to give the overall change in internal energy. However, since $q = 0$ for the adiabatic processes:

$$\Delta U = q_H + q_L + w_I + w_{II} + w_{III} + w_{IV} \quad (\text{Carnot cycle, closed}) \quad 11.1.2$$

The total work, w , is given by:

$$w = w_I + w_{II} + w_{III} + w_{IV} \quad (\text{Carnot cycle, closed}) \quad 11.1.3$$

Since $\Delta U = 0$, the work done must be at the expense of the total heat transfer. Solving Eq. 11.1.2 for the total work:

$$w = -(q_H + q_L) \quad (\text{Carnot cycle, closed}) \quad 11.1.4$$

The efficiency of an engine is defined as the work done divided by the heat input necessary to do that amount of work:

$$\xi = \frac{-w}{q_H} \quad (\text{closed}) \quad 11.1.5$$

Substituting Eq. 11.1.4, for the total work, into the definition of the efficiency gives:

$$\xi = \frac{-w}{q_H} = \frac{q_H + q_L}{q_H} \quad (\text{Carnot cycle, closed}) \quad 11.1.6$$

Remember that the work done by a cyclic process is given by the area enclosed in the plot of P versus V . The choice of the particular steps in the Carnot cycle is to maximize this area. The equation for the efficiency, Eq. 11.1.6, is the result of the conservation of energy. You don't get something for nothing. To do work for a cyclic process, the energy must be supplied from a high temperature reservoir. Because heat flows from the high temperature reservoir into the system, the heat flow is positive, $q_H > 0$, since the transfer increases the energy of the system. Transfer of energy from the system to the low temperature reservoir is negative, $q_L < 0$, since this transfer decreases the energy of the system. Because q_L is negative, any transfer of energy to the low temperature reservoir decreases the work that can be done. Since the low temperature reservoir is often the surroundings, the transfer of energy is characterized as the loss of waste heat to the surroundings. This waste heat decreases the efficiency of the process. The only way to have a 100% efficient process is if $q_L = 0$. Our experience tells us that engines always produce waste heat; q_L cannot be zero. Automobiles have radiators that transfer waste energy to the surroundings. Coal fired and nuclear power plants discharge waste heat into nearby rivers or the ocean or use cooling towers. Waste heat seems to be a general consequence of the operation of thermal cycles. The goal of conservation, then, is to minimize q_L . Is it ever possible to have a thermal cycle that is 100% efficient?

In deriving Eq. 11.1.6, we did not specify the working substance or if the processes were reversible or irreversible. Eq. 11.1.6 is applicable to any working substance or process operating in a Carnot cycle. Since reversible processes give the maximum work on expansion and require the minimum work for contraction, a reversible Carnot cycle will give the maximum efficiency for the process, given the temperatures of the high and low temperature reservoirs. However, does the working substance change the efficiency? Is a steam-based cycle more or less efficient than a cycle based on heated air or a Freon? Carnot was very clever in setting up the steps in the Carnot cycle. The Carnot cycle is a very general model. Does any reversible Carnot cycle give the maximum work available for a given T_H and T_L ?

The Efficiency of a Reversible Carnot Cycle is Independent of the Working Substance: To determine if the Carnot efficiency depends on the working substance, we will start with our original working substance, Figure 11.1.1, and then assume that a more efficient working substance exists. We will work through the consequences and look for an inconsistency. If we find that the assumption of a more efficient working substance is consistent with our experience, we will conclude that the efficiency of a reversible Carnot cycle depends on the working substance. If we find an inconsistency, then our original assumption must be wrong, and then we must conclude that all reversible Carnot cycles have the same efficiency. We label the properties of the new, more efficient Carnot cycle with primes, Figure 11.1.2. The assumption is that $\xi' > \xi$, in other words the new, primed system is more efficient than the original unprimed system.

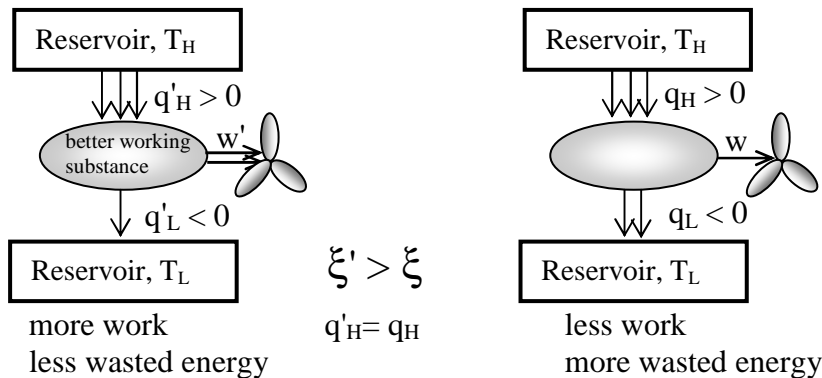


Figure 11.1.2: Assume the primed system has a working substance that gives a higher efficiency.

Next we specify that the amount of energy extracted from the high temperature reservoir for each system be the same, $q'_H = q_H$, so that we can make a fair comparison. If the primed system is more efficient, for the same amount of input energy, the primed system will produce more work while wasting less energy through heat transfer to the low temperature reservoir, $w' > w$ and $-q'_L < -q_L$. We write this last inequality as $-q'_L < -q_L$ since q'_L and q_L are both negative numbers. To help avoid confusion, we will always give comparisons between positive numbers.

Now run the less efficient cycle as a heat pump and use the more efficient cycle to drive the heat pump, Figure 11.1.3a. A heat pump is just an engine in reverse. Work is input to a heat pump, which transfers energy from the colder reservoir to the hotter reservoir.

Since the primed system is more efficient than the original system, the primed system produces more work than the original system needs to operate as a heat pump. The net result is that work is still available to do useful things. But where does the energy come from for this work? It can't come from the high temperature reservoir, because the same amount of energy is being drawn from the high temperature reservoir as is being pumped back in. The energy to pay for the work comes from the low temperature reservoir! This low temperature source is inconsistent with our experience. A simple example to show this inconsistency is to consider a steam driven boat (real examples include air craft carriers and nuclear submarines). Once the high temperature reservoir is established at T_H , no additional energy is drawn from the reservoir; that is, we wouldn't need to burn any more fuel. Instead the energy to power the vessel is extracted from the ocean. This situation doesn't violate the First Law. The energy is conserved; the energy necessary to do the work is extracted as heat from a reservoir. However, our experience tells us that boats need lots of fuel for propulsion. Extracting energy from a reservoir and the production of an equal amount of work without any other change in the system is called perpetual motion of the second kind, which our experience tells us is impossible. Our original assumption must then be incorrect. Therefore, any reversible Carnot cycle operating between the same two temperatures gives the same, maximal amount of work. The efficiency of a Carnot cycle is independent of the working substance. This independence makes the reversible Carnot cycle a very generally useful model.

All reversible Carnot cycles operating between the same two temperatures have the same efficiency. This realization also tells us something quite important. If our original cycle has an efficiency less than 100%, then all cycles between the same two temperatures will have the same less than perfect efficiency. Since we have yet to find any Carnot cycle that operates at 100% efficiency, then that must mean, in our experience, there are no reversible Carnot cycles that operate at 100% efficiency. In other words, our experience is that there is always some waste heat from thermal cycles in closed systems, no matter how carefully engineered or no matter how close to true reversibility these cycles run.

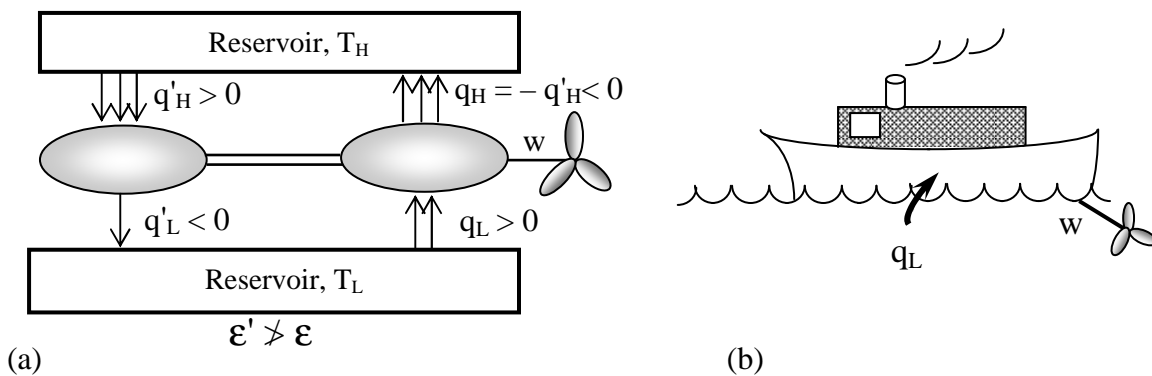


Figure 11.1.3: (a) The more efficient, primed system provides enough work to run the less efficient system as a heat pump and is still able to do useful work. No net change occurs for the energy in the high temperature reservoir. (b) Such a system would be able to do useful work by extracting an equal amount of energy from the low temperature reservoir, without any other change in the system.

The Second Law of Thermodynamics: The analysis that we just used is one of the first statements of the Second Law of thermodynamics. A careful statement of the Second Law similar to that originally given by William Thomson (Lord Kelvin) in 1853 is:¹

Principle of Thomson: It is impossible to devise an engine that working in a cycle shall produce no effect other than the extraction of heat from a reservoir and the performance of an equal amount of work.

We can also consider the operation of heat pumps as a basis for our comparison of heat and work transfers. In this mode the work output of the primed cycle is set equal to the work input of the unprimed cycle so no net work is done. The net energy flow is then the transfer of heat from the colder reservoir to the hotter reservoir. The statement of the Second Law based on this analysis is due to Rudolf Clausius:²⁻⁴

Principle of Clausius: It is impossible to devise an engine that working in a cycle shall produce no effect other than the transfer of heat from a colder to a hotter body.

What do these statements of the Second Law tell us about cyclic processes? These principles tell us that the First Law isn't the whole story. Heat and work can not be freely interconverted. Instead, Thomson's statement requires that to do useful work energy must be extracted from a high temperature reservoir and some heat must also be transferred to a low temperature reservoir. Heat transfer to the low temperature reservoir is waste heat, which decreases the efficiency of the process. The maximum efficiency of a Carnot cycle cannot be 100%, unless $q_L = 0$.

Laws are the compilation of our common observations of the world. Laws are not directly derivable, in a mathematical sense, but rather are statements of our expectations based on the experience of many people over the course of history. The principles of Thomson and Clausius are just two of many statements of the Second Law. Our goal in studying thermodynamics is to predict the spontaneity of chemical reactions. It is hard to see the relevance of these statements of the Second Law to our goals. Even though the understanding of Carnot cycles is useful in its own right, the analysis of reversible Carnot cycles historically provided the insight necessary for the definition of the concept of entropy. To continue our search for the criterion for spontaneous change, we can look at any spontaneous process. A Carnot cycle will work as well as any other process, since we seek the underlying form of nature that holds for all physical processes. To continue, we next consider a reversible Carnot cycle with an ideal gas as the working substance.

11.2 Maximum Efficiency of a Thermal Process

Ideal Gas Reversible Carnot Cycle: The efficiency of any Carnot cycle operating between the same high temperature reservoir and low temperature reservoir is the same, no matter the working substance. So we may as well use an ideal gas as our working substance to make things simple.

The heat transfer and work done for each step in the Carnot cycle are, Figure 11.2.1:

I. Isothermal, T_H	$q_H = -w_I$		
II. Adiabatic	$q_{II} = 0$	$w_{II} = \Delta U$	
III. Isothermal, T_L	$q_L = -w_{III}$		
IV. Adiabatic	$q_{IV} = 0$	$w_{IV} = \Delta U$	(Carnot cycle, closed) 11.2.1

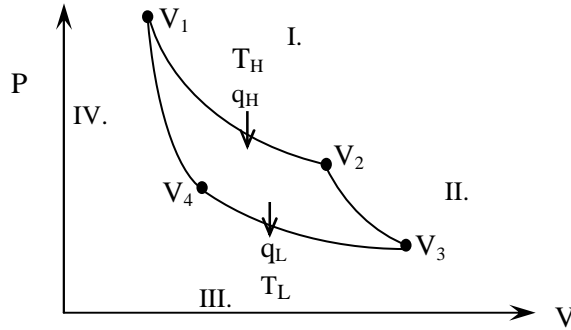


Figure 11.2.1: A reversible Carnot cycle with an ideal gas as the working substance.

and for the first isothermal step at T_H the work is:

$$\text{I. } w_I = -nRT_H \ln V_2/V_1 \quad (\text{isothermal, ideal gas, reversible, closed}) \quad 11.2.2^\circ$$

The first adiabatic step lowers the temperature from T_H to T_L and $w_{II} = \Delta U$. For any process in an ideal gas $dU = C_v dT$:

$$\text{II. } w_{II} = \int_{T_H}^{T_L} C_v dT = -\int_{T_L}^{T_H} C_v dT \quad (\text{adiabatic, ideal gas, closed}) \quad 11.2.3^\circ$$

In Eq. 11.2.3°, we invert the limits of integration and change the sign of the integral so that the limits start at the lower temperature and end at the higher. The isothermal compression at T_L begins the process of returning to the initial state:

$$\text{III. } w_{III} = -nRT_L \ln V_4/V_3 \quad (\text{isothermal, ideal gas, reversible, closed}) \quad 11.2.4^\circ$$

The final adiabatic step returns the system to the initial state at T_H :

$$\text{IV. } w_{IV} = \int_{T_L}^{T_H} C_v dT \quad (\text{adiabatic, ideal gas, closed}) \quad 11.2.5^\circ$$

The cycle is then repeated. The total work is the sum for the four steps:

$$w = -nRT_H \ln V_2/V_1 - \int_{T_L}^{T_H} C_v dT - nRT_L \ln V_4/V_3 + \int_{T_L}^{T_H} C_v dT \quad (\text{reversible Carnot cycle, ideal gas, closed}) \quad 11.2.6^\circ$$

The work for the two adiabatic steps cancels giving:

$$w = -nRT_H \ln V_2/V_1 - nRT_L \ln V_4/V_3 \quad (\text{reversible Carnot cycle, ideal gas, closed}) \quad 11.2.7^\circ$$

To simplify this equation, we suspect that there may be a relationship between V_1 and V_2 and also V_3 and V_4 , since the pairs of volumes are at the same temperature. To find a relationship between V_2/V_1 and V_4/V_3 , remember for an adiabatic process, starting at initial state V_i and P_i and ending in the final state V_f and P_f , that $V_f T_f^c = V_i T_i^c$, with $c = C_v/nR$. For the adiabatic steps in the Carnot cycle:

$$V_4 T_L^c = V_1 T_H^c \quad (\text{adiabatic, ideal gas, reversible, closed}) \quad 11.2.8^\circ$$

$$V_3 T_L^c = V_2 T_H^c \quad (\text{adiabatic, ideal gas, reversible, closed}) \quad 11.2.9^\circ$$

Dividing Eq. 11.2.8° by 11.2.9° gives the desired ratios:

$$V_4/V_3 = V_1/V_2 \quad (\text{reversible Carnot cycle, ideal gas, closed}) \quad 11.2.10^\circ$$

Substituting Eq. 11.2.10° into Eq. 11.2.7° gives:

$$w = -nRT_H \ln V_2/V_1 - nRT_L \ln V_1/V_2 = -nRT_H \ln V_2/V_1 + nRT_L \ln V_2/V_1 \quad (\text{reversible Carnot cycle, ideal gas, closed}) \quad 11.2.11^\circ$$

Collecting terms in $\ln V_2/V_1$ gives:

$$w = -nR(T_H - T_L) \ln V_2/V_1 \quad (\text{reversible Carnot cycle, ideal gas, closed}) \quad 11.2.12^\circ$$

Noting that for the heat transfer from the high temperature reservoir, $q_H = -w_1$, we can now calculate the overall efficiency by substitution of Eqs. 11.2.2° and 11.2.12° into the definition of the efficiency, Eq. 11.1.5:

$$\xi_{\max} = \frac{-w}{q_H} = \frac{nR(T_H - T_L) \ln V_2/V_1}{nRT_H \ln V_2/V_1} \quad (\text{reversible Carnot cycle, closed}) \quad 11.2.13$$

Cancelling common factors gives the final result:

$$\xi_{\max} = \frac{T_H - T_L}{T_H} \quad (\text{reversible Carnot cycle, closed}) \quad 11.2.14$$

Even though we derived this equation using an ideal gas, this equation is valid for any working substance. This equation for the maximum efficiency of a Carnot cycle is the most famous equation in thermodynamics. It is certainly one of the most useful. This equation can also be considered as a statement of the Second Law of thermodynamics. Notice that the efficiency of a Carnot cycle improves as the difference in temperature increases. The difference in temperature between the two reservoirs is called the temperature gradient; the temperature gradient drives the conversion of heat into work. The larger the gradient, the more efficiently heat can be converted into work. Therefore, the higher the temperature of the hot reservoir, the more useful that energy is. In a sense, energy in the high temperature reservoir has a higher quality. Energy released into the low temperature reservoir, which is usually the surroundings, has a diminished ability to do useful work. Energy in the low temperature reservoir is lower in quality. The maximum efficiency can be 100% only when the low temperature reservoir is at 0 K, which we will see from the Third Law of thermodynamics, is impossible. The limited efficiency of real cycles means that not all of the energy of the universe can be converted into useful work.

Practical Energy Production and Conservation: The internal combustion engine in an automobile is adequately modeled as a Carnot cycle. Even though the flame temperature of burning gasoline reaches ~3000 K, the effective gas temperature at the peak energy transfer point of the compression cycle is much lower, around ~530 K. For an ambient temperature of 300 K, the maximum Carnot efficiency between 530K and 300 K is:

$$\xi_{\max} = \frac{T_H - T_L}{T_H} = \frac{530 - 300}{530} = 0.434 \quad (\text{reversible Carnot cycle, closed}) \quad 11.2.15$$

That is, only 43%. This sizeable inefficiency is unavoidable for an engine operating in a thermal cycle. At least 57% of the energy in a gallon of fuel is completely wasted to the surroundings.

This wasted energy is necessary to “pay” for the conversion of random thermal energy into useful work. Improvements in engineering can do nothing about the 57% loss of energy, which we will soon see is necessary for the production of entropy. The actual energy efficiency of an automobile, based only on internal combustion, is actually on the order of 20-25% when frictional losses and other inefficiencies are taken into account.⁵ Hybrid vehicles do about 25% better for highway driving than high efficiency internal combustion only cars.

If the same gallon of fuel is instead used to power a fuel cell that produces electricity, then theoretical efficiencies in the 80% range for the production of electricity are possible. Because fuel cells do not operate in a thermal cycle, they are not limited by the Carnot efficiency. However, practical fuel cell based automobile efficiencies closer to 36% are expected.⁶ Hydrogen fuel cells are expected to be less than 80% efficient because of issues surrounding hydrogen storage. However, hydrogen combustion will not contribute to global warming, if the hydrogen is not made using natural gas, oil, or coal. Unfortunately, currently the only large-scale source of hydrogen is from natural gas.

The production of transportation fuels will remain a critical issue until all-electric or hydrogen based vehicles can be efficiently produced without the use of fossil fuels for electricity production. Until then we need a greatly increased emphasis on energy conservation and new fuels. For energy conservation, thermodynamics provides a sobering message that shows we are close to the theoretical maximum efficiency already. That is not to say that efforts towards greater efficiency aren't necessary. A 50% improvement in fleet average gas mileage is an important first step in moving towards energy independence and the decrease of greenhouse gases. However, a 50% improvement in gas mileage will only bring us closer to the theoretical maximum efficiency of about 40% overall. Significant decreases in energy use for transportation will require bringing all vehicles under improved efficiency standards, more effective and efficient means of mass transportation, and a significant reduction in total miles traveled.

Example 11.2.1: Carnot Efficiency

Nuclear power plants and some coal-fired power plants operate with steam in equilibrium with liquid water, so called saturated steam. The maximum temperature for saturated steam is the critical point of water, 374°C (705°F) at 221 bar (22.06 MPa, 218 atm). Standard boilers operate up to around 180 bar, giving a steam temperature of 357°C. (a) Calculate the Carnot efficiency of a power plant operating between the temperatures of 357°C and 32°C, a common exhaust temperature for an efficient steam turbine. (b) Nuclear power plants operate at a lower temperature than coal-fired plants, because the steam is made using water-to-water heat exchange using the reactor coolant.⁷ Calculate the Carnot efficiency of a power plant operating between the temperatures of 250°C and 32°C.

Answer: Converting to the absolute temperature scale, 357°C, 250°C, and 32°C correspond to 630 K, 523 K, and 305 K, giving the Carnot efficiencies of:

$$(a) \quad \xi_{\max} = \frac{T_H - T_L}{T_H} = \frac{630 - 305}{630} = 51.6\%$$

$$(b) \quad \xi_{\max} = \frac{T_H - T_L}{T_H} = \frac{523 - 305}{523} = 41.7\%$$

Nuclear power plants operate at around 38% efficiency, which is not that much less than the theoretical maximum.⁷

Example 11.2.2: Carnot Efficiency

Most coal and oil fired power plants operate on superheated steam. Superheated steam is not in equilibrium with liquid water, so the maximum temperatures are much higher. The Tennessee Valley Authority's Kingston Fossil Plant near Knoxville, Tennessee, uses superheated steam at 540°C (1000°F) at pressures of more than 124 bar (1,800 psi).⁸ The turbine discharge temperature is 32–38°C. Calculate the maximum Carnot efficiency of a modern superheated steam power plant.

Answer: Using 540°C and 35°C, or in absolute units 813 K and 308 K, gives $(T_H - T_L)/T_H$ still a disappointing 61.1% efficiency. Actual operating efficiencies are in the ~48% range for high temperature, steam based, electrical production.

Solar Energy Conversion: All objects emit light. As the temperature of an object increases the net energy produced as light increases and the frequency of maximum emission increases. This emission is called black-body radiation. Your body emits light in the infra-red region of the electromagnetic spectrum (you glow in the infra-red region of the spectrum). The temperature of the filament in an incandescent light bulb corresponds to around 3800 K. A small change in the temperature produces a large change in the light flux from an object. The total flux, which is the energy emitted per second per unit area, is given by the Stefan-Boltzmann law:

$$J_{\text{blackbody}} = \sigma T^4 \quad 11.2.16$$

where σ is the Stefan-Boltzmann constant, $5.6704 \times 10^{-8} \text{ W} \cdot \text{m}^{-2} \cdot \text{K}^{-4}$ and $1 \text{ W} = 1 \text{ J s}^{-1}$. Most all of the available energy on the earth, other than nuclear and geothermal energy, derives from the sun. The equivalent black-body surface temperature of the sun is 5800 K. This energy drives photosynthesis, the water cycle, and wind generation. The water cycle gives rise to hydroelectric power, and wind generation gives rise to wind turbine based energy production. Fossil fuels are the result of photosynthetic energy production that has been stored over geologic time.

Trees and other conventionally grown crops are only about 1% efficient in converting solar energy into biomass.⁹ The total world efficiency for solar conversion to biomass is estimated to be 0.13-0.17%.⁹ The direct conversion of solar energy into useful chemical fuels can more efficiently utilize the energy from the sun. Many processes have been proposed that convert solar energy into electricity or fuels, especially hydrogen.

Photosynthesis and Photovoltaic Energy Conversion: Even though photosynthesis, photovoltaics, and solar thermal production are steady state processes, the limiting efficiency can still be compared to the corresponding Carnot efficiency.¹¹ The maximum efficiency of direct solar processes, such as photochemistry, photosynthesis, and photovoltaic cells, is the corresponding Carnot efficiency for the process operating between the surface temperature of the sun, 5800 K, and ambient temperatures:

$$\xi_{\max} = \frac{T_H - T_L}{T_H} = \frac{5800 - 300}{5800} = 94.8\% \quad 11.2.17$$

In the case of photovoltaic cells, electrons are the working substance and the inefficiency results from the backwards flow of electrons through the device driven by the ambient available thermal kinetic energy, RT_L . Photovoltaics also suffer radiative loss as the solar cell surface temperature increases above the ambient, given by Eq. 11.2.16. One significant additional limiting factor for photovoltaics or photosynthesis is that neither process utilizes the full emission spectrum of the sun. The photosynthetically active radiation, or PAR, is in the range of 380-710 nm, which is about 50% of the total solar flux.¹² The practical limiting efficiencies for direct solar energy conversion in photosynthesis and photovoltaics are about 20%.^{13,14}

It may seem strange to consider absorption of light from the sun in this fashion. However, referring to Figure 11.1.1, note that heat transfer, in general, occurs by conduction, convection, and radiation. Energy transfer from the sun is just all in radiation. Since the energy transfer pathway in Figure 11.1.1 need not be specified, the transfer may be remote through convection or radiation as well as through direct conductive contact.



<https://share.sandia.gov/news/resources/releases/2004/renew-energy-batt/Stirling.html>

Figure 11.2.2: Stirling engine based electricity production using solar-dish concentration at Sandia National Laboratory. The system gives a solar-to-electric conversion efficiency reaching 30 percent. Each unit can produce up to 25 kilowatts of daytime power.¹⁰

Solar Thermal Cycles: Solar thermal processes convert the energy of the sun into thermal energy in an absorbing medium, Figure 11.2.2. Solar thermal cycles can more efficiently use the full spectrum of the sun than photovoltaics or photosynthesis. Many thermal cycles have been proposed that use this thermal energy to produce useful fuels. The direct dissociation of water at

temperatures greater than 2500 K using solar mirror concentration has been proposed for the production of hydrogen. Even at 2700 K the extent of the dissociation of water lies far to the left:



However, separation techniques, including effusion, may be useful for extracting H_2 in a steady state, non-equilibrium continuous process. Even though solar thermal production is neither at equilibrium or a closed process, the limiting efficiency can still be compared to the corresponding Carnot efficiency. Consider a cyclic process that uses energy extracted from a solar absorber, Figure 11.2.3. The maximum efficiency of solar thermal processes is estimated as the corresponding Carnot efficiency for the process operating between the absorber temperature, T_H , and ambient temperatures, T_L , just like any Carnot cycle:

$$\xi_{\max} = \frac{T_H - T_L}{T_H} = \frac{2500 - 300}{2500} = 88\% \quad 11.2.19$$

which is a tantalizing improvement over plant based photosynthesis.

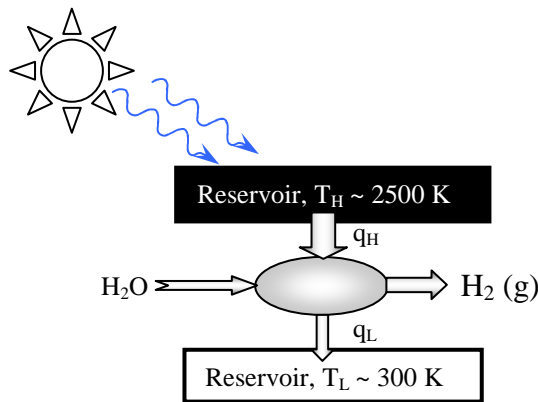


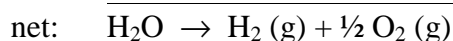
Figure 11.2.3: A Concentrating Solar Power, CSP, system heats an absorber to a high temperature. The solar flux provides the energy to the high temperature reservoir for a chemical process that operates in a cycle, produces hydrogen or other fuel, and discharges waste energy to the surroundings.

Additional inefficiencies result when the energy of the system is lost as black-body radiation to the surroundings at the characteristic temperature of the process.^{15,16} Let the total solar flux into the process be given as J_{solar} . The efficiency for solar thermal processes including the Carnot efficiency and radiative loss at the absorber at temperature, T_H , using Eq. 11.2.16 is:

$$\xi_{\max} = \left(\frac{T_H - T_L}{T_H} \right) \left(\frac{J_{\text{solar}} A - a \sigma T_H^4}{J_{\text{solar}} A} \right) \quad 11.2.20$$

where A is the solar collector area and a is the area of the absorber. This radiative energy loss from the surface of the absorber greatly decreases the efficiency at higher temperatures. The efficiency peaks at around 75% for temperatures in the 1500 – 2000 K range. Finding chemical reactions that generate hydrogen from water efficiently at temperatures below 2000 K is an important challenge.

Thermochemical water-splitting cycles produce hydrogen from water at much lower temperatures than the direct process, Eq. 11.2.18.¹⁷ The Sulfur-Iodine cycle consists of three coupled reactions, which add to give the dissociation of water:



These three reactions constitute a catalytic cycle operating in a steady state. All the reactants, other than water, are regenerated and recycled. Thermal energy is required for the endothermic high-temperature dissociation of sulfuric acid. Energy is dispersed to the surroundings through the low temperature exothermic processes. In the Sulfur-Iodine cycle most of the input energy goes into the dissociation of sulfuric acid. This thermochemical cycle can use concentrating solar power, nuclear, or any other high temperature energy source. The development of new thermochemical cycles is one way chemistry can make a central contribution to energy security and the amelioration of greenhouse gas emission.

The highest practical conversion efficiency of solar energy into electricity may be the use of solar concentrator based Stirling engine driven electrical generation.^{10,18} Stirling engines are external heat source engines, Figure 11.2.2. Helium or hydrogen, which has the highest thermal conductivity of any gas, is used as the working substance. Stirling engines are heavier than internal combustion engines, but their high relative mechanical efficiencies make Stirling engines ideal for stationary applications like solar energy conversion. Stirling engines operate in a closed cycle, which is limited by the Carnot efficiency.¹⁶ Typical Stirling engines operate at 700°C, giving a Carnot efficiency of 68%.^{16,18} The chemical aspects of research in this area are in materials science for developments in solar collector fabrication and high temperature materials. This efficiency is also a useful comparison benchmark when considering chemical solar thermal cycles.

11.3 Thermodynamic Definition of Entropy; Entropy Measures the Dispersal of Energy

Carnot was very clever in creating the Carnot cycle as a general model for cyclic thermal processes. The Carnot cycle is independent of the working substance and is maximal for reversible processes. This behavior is universal for all systems operating in a thermal cycle. The Carnot efficiency incorporates a general principle of the physical world. However, in thermodynamics we usually prefer to express our description of a process in terms of state functions and in terms directly related to the internal energy change for the process. Let's see if we can recast the Carnot efficiency into terms that are useful for evaluating the spontaneity of chemical reactions and phase transitions. Consider a general Carnot cycle. The efficiency is given as, Eq. 11.1.6:

$$\xi = \frac{-w}{q_H} = \frac{q_H + q_L}{q_H} \quad (\text{any Carnot cycle, closed}) \quad 11.3.1$$

For a reversible Carnot cycle, Eq. 11.2.14 also holds and then $\xi = \xi_{\text{max}}$ giving:

$$\frac{q_H + q_L}{q_H} = \frac{T_H - T_L}{T_H} \quad (\text{reversible Carnot cycle, closed}) \quad 11.3.2$$

This relationship shows, quite surprisingly, that the heat transfers from the high temperature reservoir and to the low temperature reservoir are not independent. The heat transfers are directly and exclusively related to the temperatures of the reservoirs. As a consequence, except when $T_L = 0$, energy is always necessarily wasted into the low temperature reservoir. In other words, the high quality energy from the high temperature reservoir is dispersed into the surroundings. Why does this transfer of heat necessarily happen?

Dividing by the denominators in Eq. 11.3.2:

$$1 + \frac{q_L}{q_H} = 1 - \frac{T_L}{T_H} \quad (\text{reversible Carnot cycle, closed}) \quad 11.3.3$$

Cancelling the constant and cross-multiplying to collect terms for the same reservoir:

$$\frac{q_L}{T_L} = - \frac{q_H}{T_H} \quad (\text{reversible Carnot cycle, closed}) \quad 11.3.4$$

and rearrangement finally gives a relationship that links the heat transferred from a given reservoir with the temperature of that reservoir:

$$\frac{q_L}{T_L} + \frac{q_H}{T_H} = 0 \quad (\text{reversible Carnot cycle, closed}) \quad 11.3.5$$

The heat transferred to or from the reservoir is dependent on the reservoir temperatures. This equation is also the sum of q/T around the full cycle, since $q = 0$ for the adiabatic steps. Whenever the sum of a function around a closed cycle is zero, it is suggestive that the function may be a state function. After this same detailed analysis of the Carnot cycle, Clausius proposed the definition for the entropy:^{3,4}

$$S \equiv \frac{q_{\text{rev}}}{T} \quad (\text{reversible process, closed}) \quad 11.3.6$$

which Eq. 11.3.5 shows is a state function for the Carnot cycle. The differential form for the definition of the entropy is:

$$dS \equiv \frac{dq_{\text{rev}}}{T} \quad (\text{reversible process, closed}) \quad 11.3.7$$

The restriction that the heat transfer must be for a reversible process is particularly important, since q/T evaluated around a Carnot cycle for an irreversible, spontaneous process is not a state function.

Thermodynamics is a very practical science. If a new concept is useful we keep it, otherwise the concept is tossed out. We need to show that entropy as defined by Eq. 11.3.6 is a useful concept. In particular, to fit into the foundations of thermodynamics, we need to show that entropy is a state function for any process, not just a Carnot cycle. Then the usefulness of entropy will be established if we can use entropy to predict the spontaneous direction for chemical reactions and other physical processes. We need to show that:

a. S is a state function for a general cycle: $\oint \frac{dq_{\text{rev}}}{T} = 0$

b. for irreversible cycles: $\oint \frac{dq}{T} < 0$

$$c. \Delta S \geq \int \frac{dq}{T}$$

d. Entropy always increases for a spontaneous process in an isolated system.

We tackle each of these steps in turn.

a. Entropy is a State Function for a General Cycle: Consider a general cycle, which is not necessarily a Carnot cycle or reversible. This general cycle may be approximated as a series of reversible Carnot cycles as diagrammed in Figure 11.3.1. The adiabatic steps between the cycles don't contribute to the dq_{rev}/T terms, since $dq = 0$ for an adiabatic process.

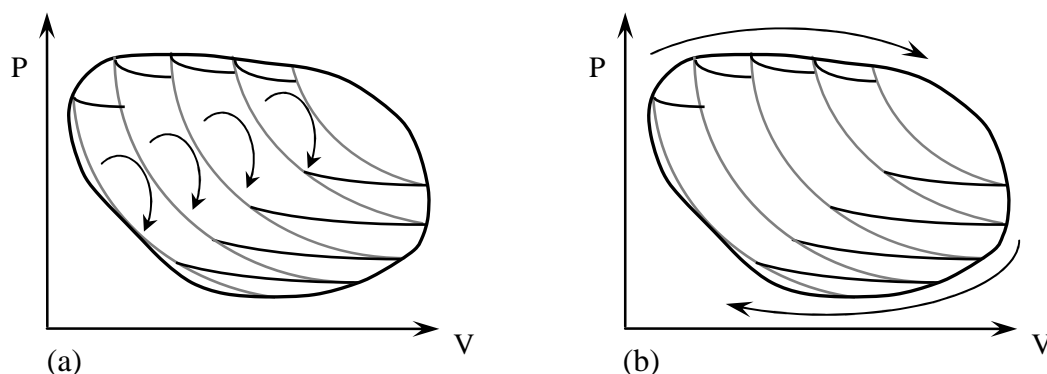


Figure 11.3.1: A general cycle may be divided into a series of N Carnot cycles. As $N \rightarrow \infty$ the general cycle is approximated arbitrarily well. (a) The sum of q_{rev}/T around each individual Carnot cycle is equal to zero, Eq. 11.3.5. (b) Summing q_{rev}/T around the general cycle is equivalent to summing over each individual cycle.

First, let the number of small cycles, N , go to infinity, $N \rightarrow \infty$. As the number of reversible Carnot cycles increases, the approximation to the general cycle gets better and better. In the limit, the approximation is arbitrarily good. Now focus on each individual reversible Carnot cycle. Using Eq. 11.3.5, the sum of q_{rev}/T is equal to zero around each small cycle, Figure 11.3.1a.

To integrate dq_{rev}/T around the general cycle, sum q_{rev}/T over all the high temperature isotherms of the Carnot cycles and then over all the low temperature isotherms, Figure 11.3.1b. This sum includes all the q_{rev}/T terms for the high and low temperatures for each individual Carnot cycle, which all sum to zero. In other words, it doesn't matter what order the q_{rev}/T terms are added: over all the high temperature isotherms and then all the low temperature isotherms around the full cycle, or alternatively around each of the individual Carnot cycles. Therefore, the sum of q_{rev}/T around the general cycle is also zero as $N \rightarrow \infty$. Mathematically,

$$\oint \frac{dq_{\text{rev}}}{T} = 0 \quad (\text{reversible, closed}) \quad 11.3.8$$

This cyclic integral is the entropy change for the cyclic process, which is equal to zero as required for a state function. This proof is central to verifying the importance of the entropy. Eq. 11.3.8 can be considered a statement of the Second Law. However, what happens for a spontaneous, irreversible process? The entropy must be calculated for a reversible path that

operates between the same initial and final states as the actual spontaneous process. Since the entropy is a state function, the entropy change is independent of the actual path of the process.

b. The Clausius Inequality Holds for Irreversible Cycles: Entropy is defined using only reversible heat transfers, $dS = \dot{d}q_{\text{rev}}/T$. But, what about $\dot{d}q/T$ for a spontaneous process? How does $\dot{d}q/T$ change for a spontaneous cyclic process? We know that the efficiency of an irreversible, spontaneous process will be less than the efficiency for a reversible process:

$$\xi < \xi_{\text{max}} \quad (\text{irreversible, cyclic, closed}) \quad 11.3.9$$

The efficiency for any Carnot process is given by Eq. 11.1.6. The efficiency for a reversible process is given by Eq. 11.2.14. Substitution into the inequality, Eq. 11.3.9, gives the relationship of the heat transfers for a spontaneous process to the heat transfers for a reversible, maximum work process.

$$\frac{q_H + q_L}{q_H} < \frac{T_H - T_L}{T_H} \quad (\text{irreversible Carnot cycle, closed}) \quad 11.3.10$$

Rearranging this equation in a parallel fashion to Eq. 11.3.3-11.3.5 gives:

$$1 + \frac{q_L}{q_H} < 1 - \frac{T_L}{T_H} \quad (\text{irreversible Carnot cycle, closed}) \quad 11.3.11$$

$$\frac{q_L}{T_L} < -\frac{q_H}{T_H} \quad (\text{irreversible Carnot cycle, closed}) \quad 11.3.12$$

$$\frac{q_L}{T_L} + \frac{q_H}{T_H} < 0 \quad (\text{irreversible Carnot cycle, closed}) \quad 11.3.13$$

which is in the same form as Eq. 11.3.5. The equality holds for reversible processes, and the inequality holds for irreversible, spontaneous processes. The corresponding differential form for an infinitesimal energy transfer is:

$$\frac{\dot{d}q}{T} < 0 \quad (\text{irreversible Carnot cycle, closed}) \quad 11.3.14$$

which holds for a spontaneous process as part of a Carnot cycle. To extend these equations to a general cycle, not just Carnot cycles, we repeat the thought process we used for Eq. 11.3.8. Approximate the general cycle as a sequence of many Carnot cycles. The sum around the general cycle of $\dot{d}q/T$ can be replaced by the sums around the individual Carnot cycles, where Eq. 11.3.13 or 11.3.14 holds for each individual Carnot cycle:

$$\oint \frac{\dot{d}q}{T} \leq 0 \quad < \text{for irreversible process} \quad = \text{for reversible process} \quad (\text{closed}) \quad 11.3.15$$

This relationship is called the Clausius inequality. The only restriction is that the process is closed. We can now use Eq. 11.3.15 to compare $\dot{d}q/T$ for a real, spontaneous process with the corresponding $\dot{d}q_{\text{rev}}/T$ for a reversible process between the same initial and final states.

c. The Clausius Inequality Compares a Real Process with the Matching Reversible Cycle: The Clausius inequality, Eq. 11.3.15, holds for a general cyclic process. How can we use the Clausius inequality to compare a non-cyclic spontaneous process to the corresponding reversible process? Consider a cycle that starts at the initial state, i , progresses to a final state, f , and then returns

back to the initial state to complete the cycle. The Clausius inequality applies to the overall process, Figure 11.3.2. The process that we want to study is the forward process from i to f . Assume that this process is a spontaneous process. However, to complete the cycle, the process from f back to i is chosen as a reversible process.

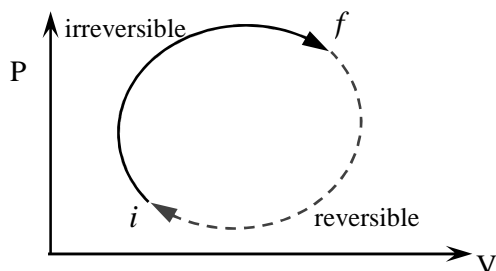


Figure 11.3.2: A general cycle that consists of an irreversible process from the initial state to a final state, and then a reversible process from the final state back to the initial state.

The cyclic integral in Eq. 11.3.15 can then be split into two integrals, one for the irreversible, spontaneous process from i to f and one for the reversible process from f to i :

$$\int_i^f \frac{\dot{d}q}{T} + \int_f^i \frac{\dot{d}q_{\text{rev}}}{T} < 0 \quad (\text{cycle, closed}) \quad 11.3.16$$

The inequality holds if any part of the cycle is irreversible. Because the return process is reversible, we can switch the integration limits and correspondingly change the sign of the integral:

$$\int_i^f \frac{\dot{d}q}{T} - \int_i^f \frac{\dot{d}q_{\text{rev}}}{T} < 0 \quad (\text{cycle, closed}) \quad 11.3.17$$

The second integral over $\dot{d}q_{\text{rev}}/T$ is defined as the entropy change for the process, ΔS :

$$\int_i^f \frac{\dot{d}q}{T} - \Delta S < 0 \quad (\text{cycle, closed}) \quad 11.3.18$$

Adding the ΔS term to both sides of the inequality gives:

$$\Delta S \geq \int_i^f \frac{\dot{d}q}{T} \quad > \text{ for irreversible process} \quad = \text{ for reversible process} \quad (\text{closed}) \quad 11.3.19$$

where the equality holds for the special case when the process is reversible, since then $\dot{d}q = \dot{d}q_{\text{rev}}$. This is the result we have been looking for. ΔS is the total change for $\dot{d}q_{\text{rev}}/T$ for the process and the right hand side is the total change in the actual $\dot{d}q/T$ for the process. The surprising fact is that for a spontaneous process the total real $\dot{d}q/T$ is always less than the corresponding reversible change, which is something that we would not have expected. This inequality is also called the Clausius inequality. The importance of the Clausius inequality is that it is completely general. This relationship is a fundamental restriction that must be true for any spontaneous process. If the integral of $\dot{d}q/T$ is evaluated for a new process and found to violate the direction of the inequality, then the process must be non-spontaneous! However, remember that the reverse of a non-spontaneous process is spontaneous. So Eq. 11.3.19 acts as a directional arrow for spontaneous processes. The spontaneous direction for any process is the direction that satisfies

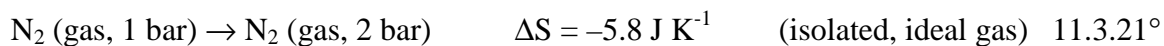
the Clausius inequality. We can recast the Clausius inequality in a simpler, but still very powerful form by focusing on isolated systems.

d. Entropy Always Increases for a Spontaneous Process in an Isolated System: The Clausius inequality is completely general. However, we can simplify our search for spontaneous processes by looking at the specific subset of processes that occur in isolated systems. For an isolated system $\dot{dq} = 0$ and the Clausius inequality, Eq. 11.3.19 reduces to:

$$\Delta S \geq 0 \quad \begin{array}{l} > \text{ for irreversible process} \\ = \text{ for reversible process} \end{array} \quad (\text{isolated}) \quad 11.3.20$$

In words, the entropy always increases for a spontaneous process in an isolated system. At first, the specific choice of an isolated system may seem to be quite restrictive. However, many processes can occur in isolated systems, including chemical reactions. We will shortly see that the specification of an isolated system is not at all restrictive for closed systems. In fact, specifying that the system is overall isolated is a useful and handy simplification that allows us to focus on the chemistry that is occurring in the process under study.

The fact that entropy always increases for a spontaneous process in an isolated system tells us how to determine if a given process is spontaneous or not. For example, the entropy change for the process where the pressure of a mole of ideal gas is doubled is negative:



In an isolated system, this process is not spontaneous, since the entropy change is negative. Rather, the reverse is the spontaneous direction. A gas at high pressure spontaneously expands to give a gas at low pressure, such as when a balloon bursts. Of course, this example is just the beginning. In particular, the universe may be considered as an isolated system for many practical circumstances, and then Eq. 11.3.20 can be phrased as: the entropy of the universe is always increasing. Entropy is the criterion for spontaneous change, in isolated systems.

11.4 Summary – Looking Ahead

Entropy and the Carnot Cycle: We can now relate the concept of entropy to the Carnot cycle. No engine can be 100% efficient because the conversion of heat exclusively into work is not an entropically allowable process. Work is essentially organized, concentrated energy. To pay for the production of work, energy must be dispersed by transfer of waste heat into the surroundings. However, from the definition of entropy, $dS = \dot{dq}_{\text{rev}}/T$, the temperature of the transfer is in the denominator of this expression. Therefore, for a given heat transfer, \dot{dq}_{rev} , the change in entropy is greater when the transfer takes place at low temperature rather than high temperature. This dependence means that the transfer of energy q_L into the low temperature reservoir can give a net increase in entropy and still have some energy left over, $q_H + q_L$, for useful work.

Entropy is the key concept in understanding the interrelationships of chemical systems to their surroundings. Our analysis of the efficiency of thermal processes shows that all of the energy of the universe cannot be converted into useful work. In the next chapter we calculate the entropy change for a wide variety of processes including phase transitions and chemical reactions.

Chapter Summary

1. Fuel bioplantations, food croplands, and forests compete for soil resources and water.

2. Poor farming practices contribute to deforestation, especially through soil depletion.
3. Deforestation contributes to global climate change.
4. Steam engines are examples of processes that operate as thermal cycles, which convert heat transfers into useful work.
5. All engines extract energy by heat transfer from a high temperature reservoir, do work, and deposit waste energy by heat transfer into a low temperature reservoir.
6. The low temperature reservoir for thermal cycles is usually the surroundings.

7. The efficiency of a process is: $\xi = \frac{-W}{Q_H}$

8. The efficiency of a Carnot cycle, reversible or irreversible: $\xi = \frac{-W}{Q_H} = \frac{Q_H + Q_L}{Q_H}$

9. The efficiency of a reversible Carnot cycle is independent of the working substance.

10. The Second Law of Thermodynamics–Principle of Thomson: It is impossible to devise an engine that working in a cycle shall produce no effect other than the extraction of heat from a reservoir and the performance of an equal amount of work.

11. The Second Law of Thermodynamics–Principle of Clausius: It is impossible to devise an engine that working in a cycle shall produce no effect other than the transfer of heat from a colder to a hotter body.

12. All reversible Carnot cycles operating between the same two temperatures have the same efficiency:

$$\xi_{\max} = \frac{T_H - T_L}{T_H}$$

13. The Stefan-Boltzmann law describes the loss of energy of an object through radiation:

$$J_{\text{blackbody}} = \sigma T^4$$

14. The practical limiting efficiencies for direct solar energy conversion in photosynthesis and photovoltaics are about 20%.

15. The solar thermal efficiency including the Carnot efficiency and radiative loss is:

$$\xi_{\max} = \left(\frac{T_H - T_L}{T_H} \right) \left(\frac{J_{\text{solar}} A - a \sigma T_H^4}{J_{\text{solar}} A} \right)$$

where A is the solar collector area and a is the area of the absorber.

16. The definition of the entropy change for a closed process is $S \equiv \frac{q_{\text{rev}}}{T}$ or $dS \equiv \frac{dq_{\text{rev}}}{T}$

17. S is a state function for a general cycle: $\oint \frac{dq_{\text{rev}}}{T} = 0$

18. The Clausius Inequality: for irreversible cycles, $\oint \frac{dq}{T} < 0$

19. The Clausius Inequality can also be written: for a general process, $\Delta S \geq \int \frac{dq}{T}$

20. Entropy always increases for a spontaneous process in an isolated system.

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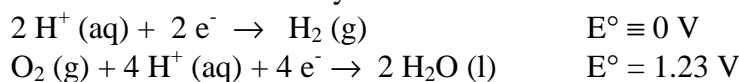
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Problems: The Thermodynamic Definition of Entropy

1. Calculate the Carnot efficiency of a solar concentrator–Stirling engine system that operates at 700°C and 37°C .
2. Is it more efficient to fly in the summer or winter?
3. On a really hot day, is it possible to cool the kitchen by opening the refrigerator door?
4. One mole of an ideal monatomic gas is used as the working substance for a reversible Carnot cycle. The initial temperature is $500. \text{ K}$ and the initial volume is 4.00 L . For step I, the gas expands to twice its initial volume. In step II the temperature is lowered to $300. \text{ K}$. What is the volume after step II, V_3 , and after step III, V_4 ? Step IV returns the system to the initial temperature and volume.
5. One mole of an ideal monatomic gas is used as the working substance for a reversible Carnot cycle. The initial temperature is $500. \text{ K}$ and the initial volume is 4.00 L . For step I, the gas expands to twice its initial volume. In step II the temperature is lowered to $300. \text{ K}$ (see problem 4). Notice that for a reversible cycle, the work done in steps II and IV is equal, but opposite in sign. (a) Calculate the work done in step I and step III. (b) Calculate the energy transferred from the high temperature reservoir, q_H . (c) Calculate the efficiency for the cycle.
6. A 0.200-mol sample of a monatomic ideal gas is used as the working substance in a reversible Carnot cycle that operates between 700 K and 300 K . The starting volume is 0.500 L . The heat transferred into the gas from the high temperature reservoir is $1000. \text{ J}$. (a) Calculate q , w , ΔU , and ΔS for each of the steps in the Carnot cycle. (b) Calculate q , w , ΔU , and ΔS for the complete cycle.
7. The peak sun solar flux that reaches a surface pointed directly at the sun is about 1.00 kW m^{-2} . Using a solar collector of area 10.0 m^2 , calculate the collector temperature that would be necessary to produce 4.00 kW of power using a steam turbine coupled to an electric generator at peak sun flux. Assume the discharge temperature of the turbine is 35°C and that the combined steam turbine and electrical generator operate at 60.0% of the maximum Carnot efficiency (due to frictional losses, etc.). Neglect radiative losses from the solar collector absorber surface.
8. In problem 7, we neglected radiative losses from the solar collector absorber surface. Assuming the same conditions and operating temperatures as in problem 7, calculate the output power when radiative losses from the solar collector absorber surface are taken into account. Assume that the absorber surface is 0.1 m^2 (this concentration ratio is $A/a = 100$).
9. Give a rough sketch of the progress for a reversible Carnot cycle on a plot of entropy versus temperature. Label the steps I-IV so that you can compare with Figure 11.2.1. Also indicate the starting point.
10. The solar concentration ratio of a solar collector is defined as the total collector area divided by the absorber area, $c = A/a$. The solar collection area for a very large “power tower” is on the order of $200. \text{ m}^2$. For a small solar absorber area of 0.1 m^2 ($\sim 1 \text{ ft}^2$), the corresponding

concentration ratio is 2000. Plot the solar thermal efficiency for this concentration ratio as a function of absorber temperature, T_H , including the Carnot efficiency and radiative losses. Assume that the low temperature reservoir for the solar thermal process is at 300. K and the solar flux is $1000. \text{ W m}^{-2}$.

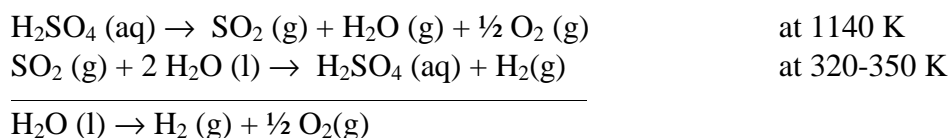
11. The electrolysis of water is a potential source of hydrogen for use as a transportation fuel. However, H_2 production is very costly. From your General Chemistry course, you might remember that the direct electrolysis of water is based on the two standard reduction half-cells:



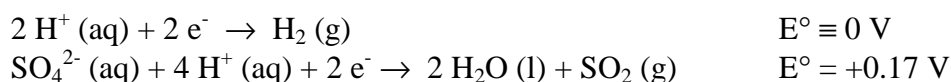
with the standard cell potential:



This cell potential is large and unfavorable. The Westinghouse-S cycle was developed in the 1970's to use solar thermal energy to lower the cost of the production of hydrogen.¹⁷ The Westinghouse-S cycle consists of two reactions, the net result of which is the production of H_2 :



The first step, the dehydration of sulfuric acid, is run in a concentrating solar collector. The second step is run in an electrolytic cell with the standard reduction half reactions:



giving the standard cell potential $E^\circ_{\text{cell}} = E^\circ_{\text{cathode}} - E^\circ_{\text{anode}} = -0.17 \text{ V}$. Even though this cell potential is still negative, the energy requirement is greatly diminished from the direct hydrolysis. Of course, electrical energy is required to run the second step, which must be obtained from conventional sources. The solar thermal efficiency for this process covers only the production of $\text{SO}_2 (\text{g})$. (a) Calculate the change in enthalpy for both steps in the Westinghouse-S cycle. (b) Calculate the maximum solar thermal efficiency for the production of $\text{SO}_2 (\text{g})$ for the thermal part of the process operating between 1140 K and 350 K. Neglect radiative losses. (c) Calculate the electrical work necessary to produce one mole of H_2 for E°_{cell} at -1.23 V and -0.17 V . [Hint: for electrochemical cells z_i is given by the number of electrons transferred in the balanced cell reaction.]

12. In Eq. 11.2.20:

$$\xi_{\text{max}} = \left(\frac{T_H - T_L}{T_H} \right) \left(\frac{J_{\text{solar}} A - a \sigma T_H^4}{J_{\text{solar}} A} \right)$$

The second term in brackets is the correction for the efficiency caused by radiative loss from the absorber surface. This correction results from the Stefan-Boltzmann equation, Eq. 11.2.16. Derive this radiative loss correction from Eq. 11.2.16.